

RESIN-COATED STEEL SHEET FOR FUEL TANKS OF AUTOMOBILE
AND METHOD OF FABRICATING THE SAME

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BACKGROUND OF THE INVENTION

(a) Field of the Invention

The present invention relates to an unleaded surface-treated steel sheet for fuel tanks of an automobile, more specifically, a resin-coated steel sheet coated with resin solution on the surface of unleaded surface-treated steel sheet coated with chromate layer and a method of fabricating the same.

(b) Description of the Related Art

Generally, it is required that fuel tanks for storing fuel of an automobile should have resistance to corrosion on its outer surface to be exposed to the atmosphere (hereinafter, referred to as the "cosmetic corrosion resistance") as well as resistance to corrosion on its inner surface to contact fuel such as gasoline (hereinafter, referred to as the "fuel corrosion resistance").

A fuel tank is usually made by press-forming steel sheets into cup-shaped upper and lower tank bodies, and welding the bodies to each other by resistance welding method such as spot welding or seam welding, or joining method such as soldering or brazing. In this respect, because two parts are joined each other in a fuel tank, good weldability and good processibility are required for the steel sheet to be applied for use in forming fuel tanks.

A ternesheet that is a cold-rolled steel sheet plated with lead-tin alloy has widely used as a steel sheet for fuel tanks. However, the ternesheet have been limited in its use because it contains lead that causes environmental pollution.

In this connection, extensive researches have been made to develop a surface-treated steel sheet for fuel tanks without using lead.

International patent publication No.WO 00/32843 invented by the present inventors discloses a plated steel sheet that does not use lead. The above patent provides an unleaded plated steel sheet coated with resin solution on the surface of zinc or zinc-based alloy plating steel sheet coated
5 with chromate layer to improve cosmetic corrosion resistance and fuel corrosion resistance.

The resin solution used for coating the unleaded plated steel sheet is phenoxy resin as main solution in the above invention. Since the phenoxy resin has a higher glass transition temperature (Tg) than other resins, it has
10 better characteristics such as cosmetic corrosion resistance and fuel corrosion resistance than epoxy, acryl or urethan resin in a flat plane part which is not subjected to process. However, while seam processing, phenoxy resin has a problem of decreasing cosmetic corrosion resistance and fuel corrosion resistance due to high glass transition temperature in a
15 processing part.

In order to improve the problem, there is a way to lower glass transition temperature of phenoxy resin, or to bond phenoxy resin layer and lower chromate layer chemically not to exfoliate the coating during seam processing.

20 Japanese Patent Laid Open Publication No. Hei2-18981 discloses a way to lower glass transition temperature of phenoxy resin. The above invention relates to a method for reinforcing a coating adhesion between resin and the lower part which bond to the resin by lowering glass transition temperature of phenoxy resin and modifying resin molecules to a rubber.
25 However, if the above method is applied to water-soluble resin, it is difficult to make water-soluble state when modifying it to a rubber, and to add rubber of water-soluble state into phenoxy resin of water-soluble state.

SUMMARY OF THE INVENTION

30 Therefore, the present invention is derived to solve the above

problems. The present invention provides a resin solution comprising additives lowering glass transition temperature of phenoxy resin without damaging physical characteristics of resin used for preparing resin-coated steel sheet.

5 It is another object of the present invention to provide a method of fabricating resin-coated steel sheet for fuel tanks of an automobile which can improve adhesion between phenoxy resin and matrix metal by using the resin solution.

10 In order to achieve the above objects, the present invention provides a resin solution comprising:

(a) a main solution of water soluble phenoxy resin having a number average molecular weight of 25,000 to 50,000;

(b) 2 to 15 phr of melamine resin on the basis of the main solution;

(c) 10 to 20 phr of colloidal silica on the basis of the main solution;

15 and

(d) water soluble ethylene-acryl resin containing 50-80% of ethylene and 50-20% of acryl resin and having a molecular weight of 20,000 to 50,000, in an amount of 5 to 15 phr on the basis of said main solution; and/or 0.5 to 3.0 phr of phosphoric ester on the basis of the main solution.

20 In order to achieve the above objects, the present invention provides a resin-coated steel sheet for fuel tanks of an automobile coated with chromate film on cold-rolled steel sheet plated with a zinc (Zn) or zinc-based alloy wherein, the resin solution comprises:

(e) a main solution of water soluble phenoxy resin having a number
25 average molecular weight of 25,000 to 50,000;

(f) 2 to 15 phr of melamine resin on the basis of the main solution;

(g) 10 to 20 phr of colloidal silica on the basis of the main solution;

and

(h) water soluble ethylene-acryl resin containing 50-80% of ethylene
30 and 50-20% of acryl resin and having a molecular weight of 20,000 to 50,000,

in an amount of 5 to 15 phr on the basis of the main solution; and/or 0.5 to 3.0 phr of phosphoric ester on the basis of the main solution,

said resin solution coated on the cold-rolled steel sheet with a coating thickness of 2–10 μm after drying the resin coating.

5 In order to achieve the above objects, the present invention provides a method of fabricating resin-coated steel sheet for fuel tanks of an automobile comprising the steps of coating the resin solution of claim 1 on steel sheet and baking drying it at 160–250°C so as to have a coating thickness of 2–10 μm . The coating process of resin solution is preferably a
10 roll-coating process.

According to the present invention, it is possible to provide a steel sheet for fuel tanks which has improved coating adhesion after processing, cosmetic corrosion resistance, and fuel corrosion resistance without using lead by preparing resin solution comprising ethylene-acryl resin and
15 phosphoric ester based on phenoxy resin. Comparing to the prior Pb-Sn plating steel sheet, the present invention can effectively prevent environmental pollution. In addition, quality of a fuel tank of an automobile is improved so that it meets to the requirement of consumers.

20 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-sectional view of a coating layer of the resin-coated steel sheet for fuel tanks of an automobile.

Fig. 2 is a diagram showing a bond between matrix metal and phosphoric ester added into resin solution.

25 Fig. 3 is a diagram of roll-coating equipment which shows coating resin solution on a cold-rolled steel sheet.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferred embodiments of this invention will be explained with
30 reference to the accompanying drawing.

As shown in Fig. 1, the resin-coated steel sheet according to the present invention has a structure that zinc or zinc-nickel is plated on a cold-rolled steel sheet and chromate which contains 100 mg/m² of chrome is treated on the plated steel sheet, and resin solution of the present invention is coated in the thickness of 2-10 μ m.

Low-carbon steel sheet having less than or equal to 0.03% of carbon content is used as the cold-rolled steel sheet in the present invention.

Zinc (Zn), zinc-nickel (Zn-Ni) alloy, zinc-cobalt (Zn-Co) alloy, zinc-manganese (Zn-Mn) alloy or zinc-chrome (Zn-Cr) alloy may be used as the plating material. In the present invention, zinc-nickel (Zn-Ni) alloy steel sheet is preferably used because it has better cosmetic corrosion resistance than that of zinc-plated steel sheet.

Chromate solution applied to zinc-nickel plated steel sheet includes a reactive type, electrolyte type, and coating type, in which coating type is preferable in terms of cosmetic corrosion resistance. When the chromate solution is applied to the steel sheet, it can be plated on one side or both sides. It is preferable to coat on both sides.

However, in case of resin solution, it can be alternatively coated on one side or both sides depending on the needs of consumer.

Such an alternation depends on the welding condition when the resin-coated steel sheet is used for manufacturing fuel tanks. That is, in case of high current condition that is easy for welding and frequent replacing of electrolyte, it is preferable to use steel sheet coated on both sides whereas in case of low current condition and infrequent replacing of electrolyte, it is preferable to use steel sheet coated on one side.

When manufacturing a fuel tank by a steel sheet coated with resin on one side, it is preferable to weld the tank by placing the coated side to face to fuel side and chromate-coated side which is not coated with resin to face to outer side. Thus, it makes welding easily because the welding electrolyte does not contact with resin part. In addition, if necessary, paint is applied to a

side which is not coated with resin in the thickness of about 100 micrometer so to reinforce corrosion resistance of fuel tank, thus, it has little influence to corrosion resistance.

Hereinafter, the resin solution used in the resin-coated steel sheet of
5 the present invention will be explained in detail.

The resin solution of the present invention is prepared by adding at least one of ethylene-acryl resin or phosphoric ester to a basic solution mixed with melamine resin and colloidal silica based on phenoxy resin as a main solution.

10 It is preferable to use a main solution of phenoxy resin having a number average molecular weight of 25,000 to 50,000. When the number average molecular weight is less than 25,000, it is difficult to have desired material properties. When the number average molecular weight is more than 50,000, it is impossible to synthesize the resin due to the limitation of
15 synthetic process.

Phenoxy resin has excellent cosmetic corrosion resistance and fuel corrosion resistance by the following reasons.

The most characteristic property of phenoxy resin is high glass transition temperature(T_g). In case of urethan, epoxy, and acryl resin, glass
20 transition temperature of these is around or less than 50°C , although it depends on the molecular weight. However, glass transition temperature of phenoxy resin is 100°C . High glass transition temperature means high movement temperature of resin chain. Thus, since the resin chains do not show Brown movement below the glass transition temperature, they have
25 primary protecting-effect against outer low molecular corrosion element such as moisture or gasoline. That is, if resin chains show Micro Brown movement, the low molecules easily infiltrate between moving chains so that corrosion elements can easily infiltrate. Therefore, resins with high glass transition temperature have screening effect against matrix metal. Particularly it shows
30 very high screening effect in a flat plane part.

Phenoxy resins, however, have the following shortcomings. That is, since resin coating is very hard, if it is subjected to process, it shows lower drawing than a resin with low glass transition temperature. In addition, since phenoxy resin has a weak adhesion with lower metal coating layer, if it is subjected to process harshly, resin coating is cracked and the adhesion of coating become weaken. Furthermore, if the resin is subjected to process more severe, resin coating exfoliates so that corrosion elements easily infiltrate into the metal coating layer of matrix metal, which results in more corrosion.

In manufacturing a fuel tank of an automobile, in order to improve formability during processing, press oil is coated before processing and then the oil is removed. However, the oil removing process makes resin hard. Thus, it cannot expect to have original screening effect because there is damage by the oil removing process in a weak adhesion point. Accordingly, it is preferable to use poly-alloy or poly-blend comprising other resin with good adhesion and drawing ratio than pure phenoxy resin.

The requirements for the other resin forming poly-blend are as follows: First, it has to have compatibility with water-soluble phenoxy resin not to result in gelation or sludge. Second, it does not have influence to the original excellent characteristics of phenoxy resin such as cosmetic corrosion resistance and fuel corrosion resistance and simultaneously it has to lower glass transition temperature of the whole resin, thereby it improves the coating adhesion.

The resin which meets the above requirements is ethylene-acryl resin.

There are two methods to add ethylene-acryl resin to phenoxy resin. One is chemical method to bond ethylene-acryl resin to phenoxy resin. The other is physical method. The physical method is preferable.

Since ethylene-acryl resin used in the present invention is synthesized in gas phase and already water-soluble state, it is impossible to synthesize phenoxy resin of water-soluble state and ethylene-acryl resin of water-

soluble state. This is why the chemical method is not appropriate in the present invention.

Ethylene-acryl resin used in the present invention has molecular weight of 20,000 – 50,000. This includes 50 – 80 % of ethylene and 50 – 20 % of acryl resin. If acryl resin is comprised less than 20 %, it is impossible to make a soluble state whereas If acryl resin is comprised more than 80 %, the glass transition temperature becomes high and adhesion becomes poor. The content of ethylene-acryl resin is preferably 5 – 15phr(parts per hundred resin). If the content is less than 5phr, coating adhesion effect is less whereas if more than 15phr, fuel corrosion resistance decreases. Since gasoline is a typical carbohydrate compound of carbon and hydrogen, it has very similar structure to ethylene resin comprising carbon and hydrogen, thus gasoline penetrates into ethylene-acryl resin and then is swelled. This is the reason that the fuel corrosion resistance decreases.

In order to improve coating adhesion of resin, there is a method to introduce additives other than making poly-blend.

The role of additives reinforces adhesion between phenoxy resin and lower chromate layer during seam processing. Mechanism of phosphoric ester of the additive used in the present invention is explained referring fig. 2.

Fig. 2 shows molecular structure of phosphoric ester. Hydroxyl group of phosphoric ester forms hydrogen-bond with hydrogen atom of water molecule, which prevents infiltrating of moisture and improves cosmetic corrosion resistance. Oxygen of phosphoric ester bonds with metal ion of surface layer and improves coating adhesion.

The content of phosphoric ester is preferably 0.5-3.0phr on the basis of phenoxy resin. If content of phosphoric ester is less than 0.5phr, the effect of adhesion decreases. If content of phosphoric ester is more than 3.0phr, there is no effect according to the increase of amount.

In order to complement shortcoming of phenoxy resin, it is possible to combine both ethylene-acryl resin and phosphoric ester or combine

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fuel corrosion resistance according to increase of the thickness as well as weldability decreases.

Baking temperature after coating the resin solution is preferably 160-250°C based on metal temperature(MT). If baking temperature is less than 5 160°C, hardening reaction of the resin is not sufficient to have cosmetic corrosion resistance and fuel corrosion resistance. On the contrary, if the baking temperature is more than 250°C, hardening reaction does not occur any longer and loss of calories increases.

Coating processes of steel sheet include roll coating, spray, 10 impregnation and so on. It is preferably to use roll coating process in the present invention.

Fig.3 shows roll coating equipment used for treating chromate and coating resin solution. The coating process according to fig.3 comprises dipping resin in a drip pan into pick-up-roll(P.U.R), transferring it by a 15 transfer-roll(T.F.R), dipping it into steel sheet in the applicator-roll(A.p.R), and drying in the oven. The amount of resin attached to the steel sheet is regulated by each roll driving direction, rolling speed, and each roll adhesion pressure.

In the present invention, the above roll coating process can be 20 applicable to one side or both sides of steel sheet.

Now, preferred embodiments are suggested to help the apparent understanding of the present invention. The below embodiments are provided for the sake of clear understanding only and the present invention is not limited thereto.

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Embodiment

Example 1

A composition of phenoxy resin with number average molecular weight of 50,000, 5 phr of melamine resin as a hardener, 15 phr of colloidal 30 silica with particle size 20nm and 2phr of wax is referred to as a standard

solution composition unless other specific note. In addition, the following method is referred to as a standard method of manufacturing steel sheet: treating chromate on electric zinc and zinc alloy plated steel sheet with plate amount of 30g/m², baking drying so as to make metal temperature of 160°C, cooling it, coating resin solution prepared by various composition, baking drying so as to make metal temperature of 190°C, and forming resin-coated steel sheet with dried coating thickness of 3μm.

After preparing resin solution by mixing ethylene-acryl resin of which weight ratio is 80:20 of ethylene to acryl with the above standard solution according to the content of below table 1, the resin-coated steel sheet was manufactured by coating the resin solution on the steel sheet plated with zinc of 20-30g/m² and treated with chromate of 100mg/m² by roll-coating process, baking drying so as to make metal temperature of 190°C, water-cooling and forming resin-coated steel sheet with dried coating thickness of 3μm.

The cosmetic corrosion resistance of the steel sheet prepared by the above process was measured in a processing part by using a salt spray test. A specimen for measurement was prepared by cutting flat plane into 95mm, preparing a cup with diameter of 50mm and height of 25mm, taking out the cup from salt spray after 500 hours, washing with distilled water and drying. According to the amount of occurrence of rust, the grades of cosmetic corrosion resistance were classified in the following way and table 1 showed the result.

Circle in circle (◎): The area of occurrence of white rust is 5% or less with respect to the total area of a specimen.

Circle (○): The area of occurrence of white rust is in the range of 5-30% with respect to the total area of a specimen.

Square (□): The area of occurrence of white rust is in the range of 30-50% with respect to the total area of a specimen.

Triangle (△): The area of occurrence of white rust is in the range of 50-100% with respect to the total area of a specimen.

In addition, in order to measure coating adhesion after processing, two types of mode were used. The first mode was to measure exfoliated area of resin after detaching cellophane tape that was attached to around of cup specimen with diameter of 50mm and height 25mm cut from flat plane of 95mm. The second mode was to measure the same method as the first mode after applying ultrasound to 10% caustic soda solution for 3 minutes at 50°C and washing. Then, coating adhesion was measured according to the below grades and table 1 showed the result.

Circle in circle (◎): The exfoliated area is 0%.

10 Circle (○): The exfoliated area is 1-5%.

Square (□): The exfoliated area is 5-10%.

Triangle (△): The exfoliated area is 10-20%.

X: The exfoliated area is more than 20%.

Fuel corrosion resistance was measured as follows: A flat plane facing to fuel is cut into 95 mm, and formed to cups with diameter of 50 mm and height of 25 mm. Three kinds of solution of 25ml were poured into the cups. Thereafter, the opening portions of the cups were covered with transparent glass plates by interposing circular "O" rings and fixed with clamp to prevent gasoline from leaking. The solutions were classified into A type, B type and C type. For the A type solution, regular gasoline was mixed with 5% of sodium chloride (NaCl) aqueous solution. For the B type solution, regular gasoline was mixed with 0.2% of sodium chloride. For the C type solution, 85% of regular gasoline was mixed with 14% of methanol and distilled water containing 60ppm of formic acid and 20 ppm of Cl⁻ ion.

25 In order to simulate driving situation of automobile, rocking equipment was used such that the solution contained in the cup was in rocking motion. The cups were allowed to stand for 4 months. Then, the cups were taken out, washed by distilled water, and dried. According to the amount of occurrence of rust, the grades of fuel corrosion resistance were classified in the following way and table 1 showed the result.

Circle in circle (⊙): The area of occurrence of white rust is 5% or less with respect to the total area of a specimen.

Circle (○): The area of occurrence of white rust is in the range of 5-30% with respect to the total area of a specimen.

5 Square (□): The area of occurrence of white rust is in the range of 30-50% with respect to the total area of a specimen.

Triangle (△): The area of occurrence of white rust is in the range of 50-100% with respect to the total area of a specimen.

X: Red rust occurred.

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Table 1

Ex. No.	Main solution	Additive		Hardener		Qualification measurement after processing			
	Type	Type	content	Type	content	Coati ng adhe sion	Cosmetic corrosion resistance	Fuel corrosi on resistan ce	
Com.Ex.1	phenoxy resin	Ethyl ene- acryl resin	0	Mela mine resin	5	□	○	○	
Com.Ex.2					10				
Com.Ex.3					15	△			
Com.Ex.4			3		5	○		◎	
Com.Ex.5									10
Com.Ex.6									15
Com.Ex.7			20		5	◎	□		
Com.Ex.8					10		○		
Com.Ex.9					15				
Ex.1			5		5		◎		
Ex.2			10						
Ex.3			15						
Ex.4			5		10				
Ex.5			10						
Ex.6			15						
Ex.7			5		15				
Ex.8			10						
Ex.9			15						

The above table 1 shows the result of measurement according to the various contents of ethylene-acryl resin as an additive and melamine resin as a hardener. As can be seen in table 1, when content of ethylene-acryl resin is more than 20phr, coating adhesion and cosmetic corrosion resistance is

good but fuel corrosion resistance decreases. In addition, when ethylene-acryl resin content is less than 5phr, the comparison examples show inferior characteristics to the examples of the present invention.

5 Example 2

After preparing resin solution by mixing phosphoric ester as an additive with the above standard solution according to the content of below table 2, the resin-coated steel sheet was manufactured by coating the resin solution on the steel sheet plated with zinc of 20-30g/m² and treated with
10 100mg/m² of chromate by roll-coating process, baking drying so as to make metal temperature of 190°C, water-cooling and forming resin-coated steel sheet with dried coating thickness of 3μm. After measuring same as Example 1, the result was shown in table 2.

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Table2

Ex. No.	Main solution	additive		hardener		Qualification measurement after processing			
	type	type	content	Type	content	Coating adhesion	Cosmetic corrosion resistance	Fuel corrosion resistance	
Com.Ex. A	Phenoxy resin	Phosphoric ester	0.3	Melamine resin	5	□	○	◎	
Com.Ex. B					10		□		
Com.Ex. C					15				○
Com.Ex. D			4.0		5	◎	◎		
Com.Ex. E					10				
Com.Ex. F					15				
Ex.A			0.5		5				
Ex.B			1.0						
Ex.C			2.0						
Ex.D			3.0		10				◎
Ex.E			0.5						
Ex.F			1.0						
Ex.G			2.0						
Ex.H			3.0						
Ex.I			0.5		15				
Ex.J			1.0						
Ex.K			2.0						
Ex.L			3.0						

The above table 2 shows the result of measurement according to the various content of phosphoric ester resin as an additive and melamine resin as a hardener. As can be seen in table 2, when content of phosphoric ester resin is in the range of 0.5-3.0phr, coating adhesion after processing is improved. However, when phosphoric ester content is more than 3.0phr or less than 0.5phr, the comparison examples show inferior characteristics to the examples of the present invention.

Meanwhile, when both phosphoric ester and ethylene-acryl resin as additives are mixed to the resin solution of the present invention, it shows the same or excellent effect than that of each additive is mixed as the above examples.